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## X-ray Compton Scattering from Aluminium and Silicon Crystals at Low Scattering Angles

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### Abstract

A correction is shown for the Compton scattering intensity that is calculated theoretically for free atoms, if the loosely bound outer electrons of the atoms construct the conduction or valence band in crystals, typically in the case of aluminium and silicon. The correction originates from the Pauli exclusion principle forbidding the electron in the band to make a transition to a filled state inside the band. The corrected figures satisfactorily explain the observed intensity at low scattering angles. The correction should be taken into account in analyses of diffuse scattering such as that caused by thermal vibration of crystals or by short-range order in alloys, particularly in the range of low scattering angles.

### 1. Introduction

In studies of materials by X-ray diffraction, X-rays scattered incoherently by the Compton effect are an unavoidable component that should be subtracted from the measured intensity. Especially in investigations concerning diffuse scattering, there may be a few cases in which a large part of the experimentally measured intensity is not composed of Compton scattering. Examples are measurements of temperature diffuse scattering (TDS) by thermally vibrating crystals and of modified Laue scattering by solid solutions of alloys in the process of phase decomposition. Accordingly, high accuracy is required for estimations of the Compton intensity. In fact, this article is based upon measurements of the scattering intensity at low scattering angles about a solid solution of low concentrations with short-range order (to be published elsewhere), which could hardly be understood in terms of the Compton intensity having been calculated theoretically for free atoms. Currently it may be popular to estimate the Compton scattered intensity in the measured whole intensity on the basis of the tables of Cromer & Mann (1967) and Cromer (1969), or of an analytical representation of the tables favourable to computer treatment (*e.g.* Smith, Thakkar & Chapman, 1975; Balyuzi, 1975; Palinkas & Radnai, 1976 *etc.*), provided that the Compton compo-

nent is not eliminated experimentally. It should be noted that the theoretical tables refer to each free atom. For condensed systems of atoms it seems that an adequate way of calculating the intensity of Compton scattering is not proposed. At relatively high angles, however, the intensity of the Compton scattering measured by Walker (1956*a*) about a pure aluminium single crystal, for instance, agrees well with the theoretical values mentioned above, implying the validity of the adoption of the tables in diffraction experiments at normal scattering angles. On the other hand, the measured values of Laval (1942*a*) in small-angle regions are considerably small compared with the theoretical values, given some discussions (Laval, 1942*b*; Freeman, 1959; Curien, 1968).

An investigation of Compton scattering in a positive sense has been carried out on the scattered intensity distribution relative to the scattered X-ray wavelengths (*i.e.* profile of the Compton band), which reflects the extent of the electron momenta in a solid (*e.g.* DuMond, 1933; Suzuki, 1968). Theodossiou & Vosnidis (1966) measured the Compton band of a polycrystalline lithium metal at low scattering angles exhibiting asymmetric profiles, from which they supported experimentally the theoretical prediction that an electron in the Fermi sphere contributing to the Compton process needs to obtain a high enough momentum to escape from the sphere, indicating the presence of electrons that are not recoiled because of the Pauli exclusion principle. If  $N$  is the total number of electrons in the sphere, this means the reduction of  $N$  to  $N_{\text{eff}}$ , the number of the electrons effective for the process in the sphere, consequently the scattering intensity per atom being decreased relative to the free independent atom.

Consider a free-electron gas in a metal, the Fermi energy,  $E_F$ , of which is consistent with the wave number  $k_F$ , and  $E_F = (\hbar k_F)^2/2m$ , where  $\hbar$  is Planck's constant and  $m$  is the electronic mass. If the modulus of the scattering vector is  $s$  ( $s = 2 \sin \theta/\lambda$ , where  $2\theta$  is the scattering angle and  $\lambda$  is the wavelength of the incident X-ray), the ratio of the number of electrons available for scattering to the total number,  $N_{\text{eff}}/N$ , is

$$N_{\text{eff}}/N = \frac{3}{4}(s/k_F) - \frac{1}{16}(s/k_F)^3 \quad (1)$$

in the case where  $0 \leq s \leq 2k_F$ , and  $N_{\text{eff}}/N = 1$  where  $s > 2k_F$ . Equation (1) expresses the equivalent statement to equation (3) of Walker (1956a) and the equation of Theodossiou & Vosnidis (1966). For a scatterer of the electron density of  $N/V$ ,

$$k_F = (3N/8\pi V)^{1/3}. \quad (2)$$

Simplifying the energy levels of an intrinsic semiconductor as the free-electron approximation, the radius of the filled valence band in  $k$  space is denoted by  $k_V$ , corresponding to energy  $E_V$ , and that of the bottom of the vacant conduction band by  $k_C$  (Fig. 1).  $k_V$  is given by the right-hand side of (2) and  $E_V = (\hbar k_V)^2/2m$ . If the width of the forbidden band (the energy gap) is  $E_G$ ,  $k_C^2 = k_V^2 + 2mE_G/\hbar^2$ . In these circumstances,  $N_{\text{eff}}/N = 0$  for  $0 \leq s \leq k_C - k_V$ ,  $N_{\text{eff}}/N = 1$  for  $s \geq k_C + k_V$ , and

$$N_{\text{eff}}/N = 1 - \gamma(s), \quad (3)$$

for  $k_C - k_V < s < k_C + k_V$ , where

$$\begin{aligned} \gamma(s) &= (k_C^3/2k_V^3)(1 - \frac{3}{2}\cos\phi + \frac{1}{2}\cos^3\phi) \\ &\quad + \frac{1}{2}(1 - \frac{3}{2}\cos\psi + \frac{1}{2}\cos^3\psi), \\ \cos\phi &= (k_C^2 - k_V^2 + s^2)/2k_Cs, \\ \cos\psi &= (k_V^2 - k_C^2 + s^2)/2k_Vs. \end{aligned}$$

Equation (1) corresponds to  $k_V = k_C$ .

In this study the X-ray diffuse scattering intensity at low scattering angles is measured for aluminium and silicon. Making a correction for the TDS, it is demonstrated that the resultant for each solid is explained in terms of the theoretically calculated Compton scattering intensity for the free atom multiplied by the correction of (1) for aluminium or (3) for silicon.

## 2. Experimental

A polycrystalline aluminium sheet of 99.99% purity and a silicon wafer for IC were used for the measurements. The aluminium sheet was hot-rolled down to a thickness of  $\sim 0.2$  mm, annealed at  $\sim 770$  K, and finally electro-polished using 20% perchloric acid in ethanol at 270 K. Because of the coarsened grains, there existed about ten

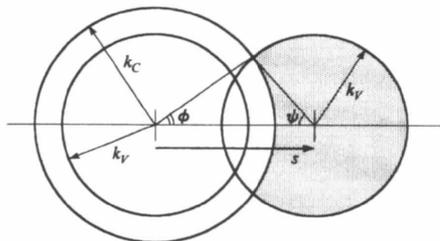


Fig. 1. Simplified  $k$ -space representation of the energy levels of an intrinsic semiconductor and the wavevector shift on Compton scattering. The electrons shifted to the shaded region contribute to the scattering.

grains in the cross section of the incident X-ray beam ( $1 \times 2.5$  mm). The single crystal of silicon of thickness  $\sim 0.4$  mm was chemically polished in a mixture of hydrofluoric acid (5%) and nitric acid (95%). The final thicknesses of the aluminium and the silicon specimen, were 0.162 and 0.180 mm, respectively.

The scattered diffuse intensity was measured photographically (Vonk & Pijpers, 1981). The range  $0.08 \leq s \leq 4.00 \text{ nm}^{-1}$  was examined with the small-angle scattering apparatus (Yamada, Sakakibara & Ohta, 1985) that attached the Guinier camera in transmission and symmetrical arrangement, the diameter of which was 103.1 mm corresponding to 1.8 mm of arc per degree in  $2\theta$ , and equipped with a Philips PW2223/20 fine-focus Cu tube operating at 40 kV and 30 mA. With the same adjustment, the scattering intensity from some gases, namely nitrogen, oxygen and air, was measured to obtain the intensity of the specimens in absolute units, electron units per atom (eua). The conversion factors of each gas were consistent within  $\pm 3\%$ . Further measurements were performed on the diffraction lines of fine aluminium powder, and it was confirmed that the blackening by the harmonics  $\lambda(\text{Cu } K\alpha_1)/2$  was 0.03% of  $\lambda(\text{Cu } K\alpha_1)$  or less.

For the aluminium specimen the measurements were made at 100 and 295 K, and for the silicon at 295 K. After the conversion in absolute units and the subtraction of the calculated intensity of the TDS, the measured Compton intensity was obtained. The TDS intensity of aluminium was calculated according to Walker (1956b) and Warren (1969). For the TDS intensity of silicon, the readings of the calculated figure of Robertson & Reid (1979) were quoted.

By using equation (2) for aluminium one obtains  $k_F = 2.8 \text{ nm}^{-1}$ , which corresponds to  $E_F = 11.6$  eV. For silicon one obtains  $k_V = 2.9 \text{ nm}^{-1}$ , which corresponds to  $E_V = 12.5$  eV (Chelikowsky & Cohen, 1976), and, since  $E_G = 1.17$  eV,  $k_C = 3.0 \text{ nm}^{-1}$ . From these values, the values of  $s$  satisfying  $N_{\text{eff}}/N = 1$  are 5.6 and  $5.9 \text{ nm}^{-1}$  for aluminium and silicon, respectively, which includes all the measured region of  $s$  in this experiment.

## 3. Results

Since the scattered X-rays in this experiment, in spite of prolonged exposure, blacken the photographic film by only 0.02–0.1 in density, errors arise mainly from inhomogeneity of the film emulsion and/or estimation of the background fog. A precision of  $\pm 0.3$  eua would be expected.

Typical results of the distribution of the measured diffuse scattering intensity of aluminium and silicon are shown in Figs. 2 and 3, respectively. The sharp increase with a decrease in  $s$  of less than  $\sim 0.5 \text{ nm}^{-1}$  may be caused by small-angle scattering due to surface imperfections (Roth, 1977). In the intensity distribution of

aluminium at 100 K (Fig. 2), peaks centred at  $s \approx 2.7 \text{ nm}^{-1}$  are diffraction lines due to condensed vacuum oil vapour on the surfaces of the cold aluminium specimen. Owing to the faint diffraction rings, it must be true that diffuse scattering from the condensed oil can be ignored in the other region of  $s$ .

The measured Compton intensity is obtained by subtraction of the calculated diffuse scattering by the phonons (Figs. 4 and 5 for aluminium and silicon, respectively). In Fig. 4 the measured values of Laval (1942a) are also cited. The thick line in the figures indicates the calculated Compton intensity of Cromer (1969) for the free atom approximated by the analytical expression of Smith *et al.* (1975), and the thin line

indicates the product of the thick line by equation (1) for aluminium or by equation (3) for silicon. The measured values coincide well with the thin line, *i.e.* the computed Compton intensity with the correction, within the error, except for the case of aluminium in the region beyond  $\sim 3 \text{ nm}^{-1}$  of  $s$  in Fig. 4. It is thought that the departure from the thin line for aluminium originated from the poor TDS estimation for a coarse-grained polycrystalline aluminium sheet.

#### 4. Discussion

Studies of the ordering and the clustering of solute atoms in alloys have been advanced elaborately by Cohen and collaborators with the aid of X-ray diffuse scattering techniques (*e.g.* Schwartz & Cohen, 1987). Concerning Compton scattering, they considered a correction in the case where the energy of the incident X-ray does not exceed the ionization energy of the *K*-shell electrons of the constituent atoms (Hayakawa, Bardhan & Cohen, 1975). This type of correction must be taken into account over the whole range of scattering angles. On the other hand, at low scattering angles as in this article, there exists many experiments of small-angle X-ray scattering on the phase decomposition of alloys, where diffuse scattering arising from the static displacement of atoms from the average lattice has a minor component compared with that due to the chemical arrangements of solute atoms on the lattice (Warren, Averbach & Roberts, 1951). In this region of scattering angles the correction for the Compton intensity described in the *Introduction* is significant.

The results of the measurements on the Compton scattering intensity in this experiment are consistent with those of Laval (1942a) for aluminium, and, including silicon, with the corrected resultant (the thin lines in Figs. 4 and 5) given by the theoretical value of Cromer (1969) (the thick lines) multiplied by equations (1) or (3). Now, it should be pointed out that the outer (valence) electrons of the atoms of an element are considered in deriving (1) and (3) as stated in the *Introduction*, while the thin lines denote the products of the theoretical Compton intensity for the free atom *as a whole* and the corrective resulting from the crystal-

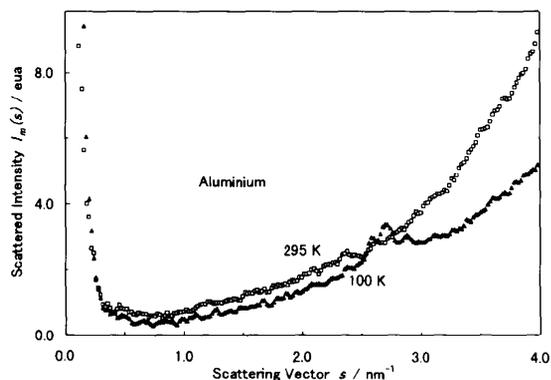


Fig. 2. Scattered intensity distribution from a polycrystalline aluminium sheet measured at 100 and 295 K.

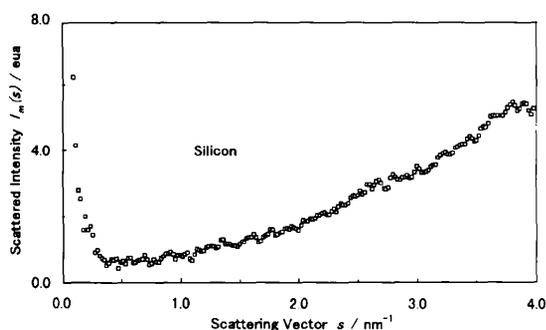


Fig. 3. Scattered intensity distribution from a silicon crystal at 295 K.

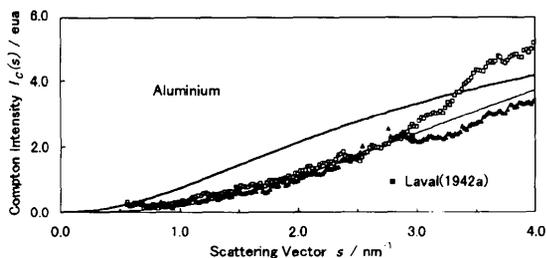


Fig. 4. Measured (open squares and triangles) and calculated (thick and thin lines) Compton scattering intensities of aluminium. The three closed squares are the measurements of Laval (1942a).

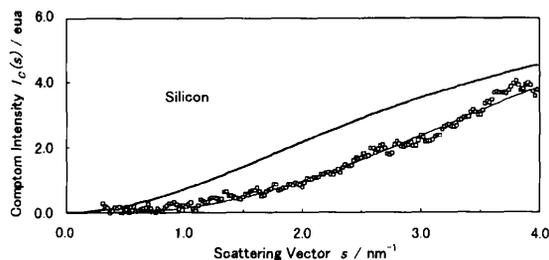


Fig. 5. Measured (squares) and calculated (thick and thin lines) Compton scattering intensities of silicon.

lization. This procedure, however, must be justified since the contribution of the electrons at the outer shells to the Compton scattering is mainly at a region of small  $s$  (e.g. Freeman, 1959), and, moreover, it is the outer-shell electrons that are influenced by the condensation of the atoms into a crystal, leaving the electrons at the inner shells almost unchanged (except for the elements of small atomic numbers). In other words, in the  $s$  range that is affected by the Pauli exclusion principle there are no serious errors in the corrected Compton intensity given by multiplying the theoretically calculated values for all electrons of a free atom by the correction factor, the small error being accentuated by the smallness of the numerical figure of the intensity.

For aluminium, as seen above, the observed and the calculated values are consistent in the small region of  $s$ . Laval (1942a) and Walker (1956a) made measurements extending to large values of  $s$ . In Fig. 6, their measured values are cited with the calculated curves, indicating good agreement over the whole range.

Some origins other than the exclusion principle forbidding a transition within the Fermi sphere have been proposed for the factor that affects the profile of the Compton band (Suzuki, 1968). They change the profile, but the integrated value, which corresponds to the total Compton intensity at a given scattering vector, is not influenced so much. In conventional and even in advanced precise X-ray crystallography, the corrective factor mentioned in the *Introduction* will satisfactorily give a good correction for the Compton intensity.

### 5. Conclusion

If the valence electrons of an atom constituting a crystal contribute to the Compton effect they must escape from the Fermi sphere, because transition within the sphere is forbidden according to the Pauli exclusion principle.

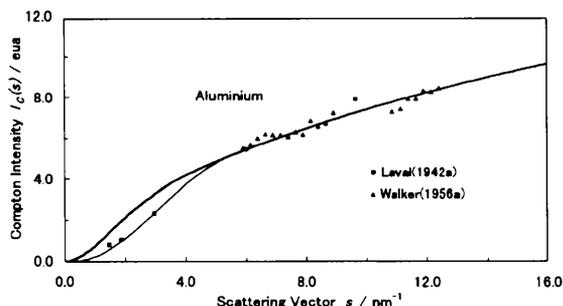


Fig. 6. Wide-range representation of experimental and calculated Compton scattering intensities of aluminium.

The minimum range of the momentum transferred from a photon on this escape corresponds to the region of the wavevector equivalent to the scattering vector at the low angle examined in this paper. In this region of scattering there existed the discrepancy between the measured Compton intensity from a crystal and that theoretically calculated for a free atom, which has not been explained satisfactorily. This difference is caused by the reduction of the electrons effective for scattering by the number that cannot escape from the sphere. In this region the Compton intensity can be predicted precisely by multiplication of the theoretical value of Cromer & Mann (1967) and Cromer (1969) by the correction factor originating from the Pauli exclusion principle.

### References

- Balyuzi, H. H. M. (1975). *Acta Cryst.* **A31**, 600–602.  
 Chelikowsky, J. R. & Cohen, M. L. (1976). *Phys. Rev. B*, **14**, 556–582.  
 Cromer, D. T. (1969). *J. Chem. Phys.* **50**, 4857–4859.  
 Cromer, D. T. & Mann, J. B. (1967). *J. Chem. Phys.* **47**, 1892–1893.  
 Curien, H. (1968). *International Tables for X-ray Crystallography*, Vol. III, pp. 247–253. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
 DuMond, J. W. M. (1933). *Rev. Mod. Phys.* **5**, 1–33.  
 Freeman, A. J. (1959). *Phys. Rev.* **113**, 176–178.  
 Hayakawa, M., Bardhan, P. & Cohen, J. B. (1975). *J. Appl. Cryst.* **8**, 87–95.  
 Laval, J. (1942a). *Compt. Rend.* **215**, 278–279.  
 Laval, J. (1942b). *Compt. Rend.* **215**, 359–360.  
 Palinkas, G. & Radnai, T. (1976). *Acta Cryst.* **A32**, 666–668.  
 Robertson, B. F. & Reid, J. S. (1979). *Acta Cryst.* **A35**, 785–788.  
 Roth, M. (1977). *J. Appl. Cryst.* **10**, 172–176.  
 Schwartz, L. H. & Cohen, J. B. (1987). *Diffraction from Materials*, 2nd ed. Berlin: Springer-Verlag.  
 Smith, V. H. Jr, Thakkar, A. J. & Chapman, D. C. (1975). *Acta Cryst.* **A31**, 391–392.  
 Suzuki, T. (1968). *Butsuri (Bull. Phys. Soc. Jpn)* **23**, 12–20. (In Japanese.)  
 Theodosiou, A. & Vosnidis, P. (1966). *Phys. Rev.* **145**, 458–465.  
 Vonk, C. G. & Pijpers, A. P. (1981). *J. Appl. Cryst.* **14**, 8–16.  
 Walker, C. B. (1956a). *Phys. Rev.* **103**, 558–561.  
 Walker, C. B. (1956b). *Phys. Rev.* **103**, 547–557.  
 Warren, B. E. (1969). *X-ray Diffraction*, ch. 11. Reading, Massachusetts: Addison-Wesley.  
 Warren, B. E., Averbach, B. L. & Roberts, B. W. (1951). *J. Appl. Phys.* **22**, 1493–1496.  
 Yamada, M., Sakakibara, A. & Ohta, M. (1985). *Mem. Sch. Eng. Okayama Univ.* **20**, 35–43.